

RMU Summer Research Project

The following paper represents the output from our summer 2005 research project. The goal of which was to produce a scientific research paper on the subject of arsenic pollution in Pennsylvania.

This work was a combined effort of Dr. Dress and Dr. Short of the department of Science at Robert Morris University. It is 15 pages long and consists of approximately 6000 words, ~ 64 references, three figures and 1 table.

Our next step is to shop this manuscript around to category A journals for peer review. The journal '[Water, Air, and Soil Pollution](#)' is first on our list.

Sincerely

Dan Short (for Bill Dress)

Outline

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Ground Water Contamination by Arsenic in South-Western Pennsylvania

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ABSTRACT -

Groundwater contamination by arsenic is one of the world's most serious environmental problems. Chronic exposure to low levels of arsenic may result in a variety of non-cancer and cancer effects. Arsenic is derived mainly from natural sources and distributed regionally according to geology and climate. At least 28 percent of Pennsylvanians depend on self-supplied groundwater as their main supply of water for domestic needs. Arsenic in Pennsylvanian groundwater supplies is generally found at concentrations $< 10 \mu\text{g}\cdot\text{L}^{-1}$ with few isolated areas in excess of the old federal standard for drinking water ($50 \mu\text{g}\cdot\text{L}^{-1}$). A higher proportion of sites (2%) exceed $10 \mu\text{g}\cdot\text{As L}^{-1}$. The maximum contaminant level for arsenic in US drinking water will be reduced to $10 \mu\text{g}\cdot\text{L}^{-1}$ by January 2006 increasing the number of known groundwater sites that do not meet the federal standard for Arsenic. A more thorough evaluation of the regions groundwater quality is suggested.

Key words: Arsenic, groundwater, contamination, drinking, water.

INTRODUCTION

Arsenic and its compounds are ubiquitous in the environment, having been used for centuries in agricultural, pharmaceutical, and construction materials. Arsenic resides in the highest category of carcinogens alongside asbestos, benzene, radon, X- and gamma radiation (IARC, 1987). It ranks #1 on the ATSDR/EPA priority list of hazardous substances (Selene *et al.*, 2003), and is considered one of the most prominent environmental causes of cancer mortality in the world (Smith *et al.*, 1992). It is also known by the epithet 'King of Poisons'.

The potential for arsenic contamination of water, air, and soil from both natural and anthropogenic sources is a significant environmental health concern. The history of the maximum contaminant level (MCL) is highly convoluted (Smith *et al.*, 2002). The current federal level of 50 parts per billion (ppb or $\mu\text{g}\cdot\text{L}^{-1}$) for arsenic in drinking water was first set by the U.S. Public Health Service in 1942. Toxicological studies published in the middle of last century (Massman and Opitz, 1954; Byron *et al.*, 1967; Mahaffey and Fowler, 1977) reported the dose-dependent effects of arsenic. Concerns over costs, the EPA's own threshold studies of low dose carcinogens, and the finding that arsenic may be an essential nutrient significantly slowed the progress of revising the standard. The emergence in 1988 of the largest mass poisoning in history affecting the inhabitants of Bangladesh and west Bengal, India associated with arsenic in contaminated groundwater has brought arsenic to the forefront of consumer's minds. Around this time the Federal Government directed the EPA to revise its drinking water regulations by 1989. Two years later the EPA revised the arsenic regulation (Wang and Wai, 2004). The MCL for arsenic will be reduced to $10\ \mu\text{g}\cdot\text{L}^{-1}$ by January 2006.

Introduction of this new standard brings the US in line with the rest of the world, in 1993 the World Health Organization (WHO) reduced their 1963 standard of $50\ \mu\text{g}\cdot\text{L}^{-1}$ setting the international standard at $10\ \mu\text{g}\cdot\text{L}^{-1}$. In 1998 the $10\ \mu\text{g}\cdot\text{L}^{-1}$ standard was adopted by the 15-member European Union (WHO, 2001). The WHO has stated that the $10\ \mu\text{g}\cdot\text{L}^{-1}$ level is not safe, although reducing it is problematic due to measurement limitations. Based on health concerns seen in the areas of the world suffering from arsenic poisoning (arsenicosis), many scientists believe this standard should be lowered even further. At the time of the revision, the EPA had originally put forward a 5 ppb drinking water standard (Smith *et al.*, 2002). In some Pacific-Asia rim countries for example the guideline standards are lower. In Australia, for example, the guideline standard is $7\ \mu\text{g}\cdot\text{L}^{-1}$.

This paper reviews the sources, environmental cycling, and contaminant levels of arsenic in various environmental compartments, in addition to surveying the levels of arsenic found locally in Western Pennsylvania.

Health Effects

The US EPA's public health warning for arsenic states that 'Some people who drink water containing arsenic in excess of the MCL over many years could experience skin damage or problems with their circulatory system, and may have an increased risk of getting cancer.' Consumption of drinking water, inhalation, ingestion, and dermal contact are the primary pathways for the bioaccumulation of As. Risk assessments have indicated the increased cancer risk to be 10 in 1000 for drinking water containing $50\ \mu\text{g}\cdot\text{L}^{-1}$, over 100 times the MCL of any other drinking water contaminant (Smith *et al.*, 2002). With a reduction to the 2006 MCL the cancer risk is now less than 3 in 1000. Drinking water is responsible for approximately 30 % of total arsenic accumulation (Appelo and Postma, 1994). In the US over 2.5 million people may have drinking water containing more than $25\ \mu\text{g}\cdot\text{L}^{-1}$ As, and 350,000 with water $50\ \mu\text{g}\cdot\text{L}^{-1}$ or more (Smith *et al.*, 1992).

According to a 1999 report by the National Research Council, chronic exposure to arsenic in drinking water may produce the following symptoms of arsenicosis: Non-cancer effects include hyper- and hypo pigmentation, keratosis, hypertension, cardiovascular diseases and diabetes; cancer end-points include skin, lung and bladder cancers (Ng *et al.*, 2003). In 2001, researchers at the Dartmouth Medical School reported that arsenic should be added to the growing list of chemicals that disrupt the endocrine system of animals (Kaltreider *et al.*, 2001). Recent evidence points to a progressive impairment of the cognitive development

of children (Wasserman et al., 2004). Arsenic is very similar chemically to its predecessor phosphorus, an essential nutrient, so much so that it will partly substitute for it in biochemical reactions, e.g. oxidative phosphorylation. Arsenic also shares similar toxicity effects with its neighbors lead and mercury, namely its high affinity for sulfur, and will interfere with protein thiols and amino acids in the human body, forming products that cause biological malfunction (Wang and Wei, 2004).

The inorganic forms of arsenic are more toxic than the organic forms and the trivalent forms are more toxic than the pentavalent forms. The approximate toxicity of arsenic compounds is: arsines > arsenite > arsenoxides > arsenate > pentavalent arsenicals > arsonium compounds > metallic arsenic. Organic forms are considered less toxic than inorganic forms. The human body methylates the ingested inorganic arsenic to monomethylarsonic acid and dimethylarsonic acid which are more rapidly excreted (Andreae, 1986). The first large-scale arsenic contamination of well waters by predominantly inorganic As(III) and (V) ($100 - 1810 \mu\text{g}\cdot\text{L}^{-1}$) and its correlation to Black Foot Disease occurred in Taiwan in the 1950's (Chiu et al., 2004). Symptoms of the disease are discoloration of the extremities from white to brown to black. A thickening and cracking of the skin leads to ulceration and eventually gangrene. Without chelation therapy, amputation is usually the only available treatment (Wai et al., 2002). Black Foot Disease has been found only in China and is believed to be a more severe form of arsenicosis, possibly expedited by malnutrition. The largest arsenic-affected population in the world is Bangladesh. In the mid 1980's a series of wells were dug in naturally arsenic rich areas, ironically in an effort to improve water quality. About half the country (53 million people) is affected with highest concentrations around 14 ppm, 300 times the WHO's guideline limit (Karim et al., 1997). Many other countries in South East Asia, such as Vietnam, Cambodia, and Tibet, are thought to have geological environments similarly conducive to generation of high-arsenic groundwaters (Ng et al. (2003).

BIOGEOCHEMISTRY

Natural/Anthropogenic Sources and Uses

Arsenic is a naturally occurring trace element found in water, air, geologic material, plants and animals. The total amount of As is estimated to be 4.01×10^{16} kg. Trace elements enter the atmosphere via both natural and anthropogenic processes (Fig. 1), the ratio for the natural to the anthropogenic atmospheric flux of As is 2:1. Natural sources of arsenic are dominated by volcanic action and the natural weathering of minerals in deep soils and rocks. There are over 200 naturally occurring arsenic minerals, the principal one of which is arsenopyrite (FeAsS). Arsenic is also added to the biosphere through anthropogenic activities such as smelting of metal ores (Chilvers & Peterson, 1987), mining, fossil fuel combustion (including the leaching of arsenic-laden ash from landfills and waste incineration), glass production, manufacture and use of pesticides and herbicides (wood preservatives), the manufacture and use of fertilizers, electronics, detergents and medicines (Matschullat, 2000).

The use of organic and inorganic arsenic as a pesticide in the USA began in the 1850s and peaked in the 1950s. In the 1960s, the use of arsenic is believed to have been 77% as pesticides, 18% as glass, 4% as industrial chemicals and 1% as medicine. Today, 70% of the world's production of arsenic is used as a wood preserving treatment, the manufacture of agricultural chemicals (pesticides, herbicides, fungicides) accounts for 22%. The remainder is used in glass, pharmaceuticals and metallic alloy production (W.H.O., 2001). The source of most concern today is the pesticide chromated copper arsenate (CCA) found in pressure treated wood. CCA timber was heavily used during the later half last century for framing structures and outdoor building material. In 1996, 73% of pressure treated lumber sold in the U.S. contained CCA. Widespread bans and use of alternative materials followed the publication of studies which showed low-level As leaching from children's playground equipment mulch, and landscape timber into surrounding soil (Kwon et al., 2004; Townsend et al. 2003, 2005). Incineration of CCA timber presents the most serious risk (Katz and Salem, 2005). Recent years have seen fatal animal poisonings, and serious human poisonings resulting from the ingestion of wood ash from CCA timber (Dube et al., 2004).

Biogeochemistry

Arsenic, a metalloid, is a redox sensitive element that occurs in the environment in the oxidation states –III, 0, III, and V. Elemental arsenic is not soluble in water, its speciation and therefore mobility in the environment is dependent on solution chemistry including Eh, pH, microbial activity, competitor ions etc. The two primary forms of minerogenic arsenic are pentavalent arsenate (which is more thermodynamically more stable and predominates under oxidizing conditions) and trivalent arsenite (which predominates under reducing conditions). Elemental arsenic is not soluble in water.

Current knowledge concerning the biogeochemical cycling and speciation of arsenic in water has been presented by Smedley and Kinniburgh (2002). General speciation in all environmental compartments has been thoroughly reviewed by Cullen and Reimer (1989). Determination of speciation includes the chemical nature of molecular compounds containing arsenic as well as the physical forms e.g. dissolved, colloidal and particulate.

Water

Dissolved forms of arsenic in the water column include arsenate, arsenite, methylarsonic acid (MMA) and dimethylarsinic acid (DMA). Arsenic concentrations found in natural (i.e. not polluted) waters range from less than $0.5 \mu\text{g L}^{-1}$ to more than $5000 \mu\text{g L}^{-1}$ in polluted areas. Arsenic levels in freshwater are typically less than $10 \mu\text{g L}^{-1}$ and frequently less than $1 \mu\text{g L}^{-1}$ (Smedley. And Kinniburgh, 2002).

Arsenic concentrations in ground water and surface waters are associated with local climate and geology. Higher levels of arsenic are usually found in groundwater rather than surface waters since groundwater stays in contact with bedrock or soil material for extensive periods. Surface water concentrations are subject to dilution by precipitation and evaporative concentration in warmer climates.

The following water quality criteria for arsenic are in use (EPA, 2001): acute exposure for freshwater Criteria Maximum Concentration (CMC) equal to $340 \mu\text{g L}^{-1}$. Chronic exposure or Criteria Continuous Concentration (CCC), equal to $150 \mu\text{g L}^{-1}$.

Air

The input, flux and residence times of arsenic are comparable to those of other trace elements in the environment such as lead, zinc and copper (Short, 1999). The total input of arsenic to the atmosphere is calculated to be of the order 10^6 kg yr^{-1} (Matschullat, 2000; Nriagu, 1979), with a mean atmospheric flux of $2 \text{ ng cm}^{-2} \text{ yr}^{-1}$. The residence time of arsenic in the atmosphere is relatively short, of the order $\sim 7\text{-}9$ days (Rahn, 1976; Walsh *et al.*, 1979). Arsenic concentrations, measured via bulk deposition of dry and wet components, found in air have been reported at levels ranging from $0.08 \mu\text{g L}^{-1}$ to $12 \mu\text{g L}^{-1}$. Its dry deposition fraction is around 10%, with a concentration range of 0.5 to 15 ng m^{-3} (Reimann and Caritat, 1998). Trace element deposition generally increases in winter, attributed to the increased frequency of temperature inversions. Arsenic has a washout factor of 640 and is mainly associated with local sources (Peirson *et al.*, 1973).

Soil/Sediments

Soil is a highly variable heterogeneous mixture. Highest As concentrations are found in highly organic soils. Concentrations of arsenic in US soils are in the range 0.1 to 55 mg kg^{-1} , with an average value of 7.2 mg kg^{-1} (Allard, 1995). Under aerobic conditions arsenic is found mainly in the form of arsenate (AsO_4^{3-}) bound to the surface of soil substrates (clay minerals, Fe/Mn Oxy-hydroxides and organics). The mobility of arsenic in the pedosphere is important when evaluating possible environmental effects. The distribution of As(V) between the solid and aqueous phases in soils has been studied extensively (Sadiq, 1997; Smith *et al.*, 1998; Zhang and Selim, 2005). The distribution coefficient (K_D) of As(V) is strongly dependent on pH and the presence of other ions, e.g. phosphate (Jain and Loeppert, 2000). Residence times for arsenic in soil are on the order of 1000-9000 years (Bowen, 1979; Hindmarsh *et al.*, 1986).

Soils in the vicinity of arsenic rich deposits, mining or smelting sites, or agricultural land may exhibit concentrations 10-20 fold higher and above the level which is considered hazardous waste by the EPA (20 ppm or mg kg^{-1}). Arsenic has been found in at least 1014 current or former NPL sites. For example in Washington State, the Everett Smelter hazardous waste site contains arsenic at 700,000 ppm (70%), 85 years after production was discontinued (OEHS, 1999; Snomish, 2001). The world-wide arsenic contents of sediments are at least 2-fold higher than in the soil. The sediment quality guidelines for the protection of aquatic biological resources are as follows: Lowest effect level (LEL) 6.0 mg kg^{-1} and a severe effect level (SEL) of 33 mg kg^{-1} (Persaud et al., 1992). Effects Range-Low (ER-L) of 33 mg kg^{-1} and an Effects Range-Moderate (ER-M) of 85.0 mg kg^{-1} (Long and Morgan, 1990). Probable effect concentration (PEC) is the level above which harmful effects are likely, for As the PEC is 33 mg kg^{-1} (Ingersoll et al., 2000).

ARSENIC IN GROUNDWATER

Arsenic in United States Groundwater

The most common exposure route of individuals to arsenic is through contaminated groundwater. Both in the US and worldwide, many populations are dependent on untreated drinking water, whether from wells, aquifers or other source. In a comprehensive, nationwide survey, Welch et al. (2000) analysed over 30,000 groundwater samples for As concentration. Approximately 50% of these samples contained $< 1 \mu\text{g As L}^{-1}$. However, almost 10% of the samples had $> 10 \mu\text{g As L}^{-1}$. Arsenic occurs in greatest concentrations in areas with high substrate arsenic associated with iron oxide minerals. Complex reactions with iron oxide and organic carbon can release As into groundwater. Several of the sites with the greatest groundwater As concentration occur in landfills and Superfund sites where the addition of organic compounds has artificially caused an increase in As dissolution.

Generally, concentrations of As in groundwater is greater in western US relative to eastern US. Welch *et al.* (2000) reported greater median As concentration in the Intermontane Plateau and Pacific Mountain System provinces compared to the other provinces examined. Arid regions (Utah, Idaho, Nevada, Utah, etc.) likely have a high degree of evaporative concentration that contributes to high As concentration in groundwater. Local mining operations for gold or other minerals is also associated with As release into groundwater. Groundwater As concentrations are also generally elevated in areas with geothermal waters. High As concentrations were measured immediately surrounding the Yellowstone geothermal system (Welch et al. 2000).

In addition to the generally greater As concentrations in groundwater in the western US, regions of relatively broad regions that exhibit consistent measurements of As concentration $> 10 \mu\text{g}\cdot\text{L}^{-1}$ occur in New England, Michigan, Minnesota, South Dakota and Wisconsin (Gooaverts *et al.* 2005, Peters and Blum 2003, Schreiber *et al.* 2000, Welch *et al.* 2000).

Arsenic in Pennsylvania (PA) Groundwater

Both the USGS (Welch *et al.*, 2000) and PA Department of Environmental Protection (Reese and Lee, 1998) have published surveys of As in PA groundwater. The USGS reported concentrations from 600 long-term groundwater monitoring sites throughout PA. Overall, the highest As concentration reported was $24 \mu\text{g}\cdot\text{L}^{-1}$ (Swistock *et al.*, 2001). The overwhelming majority (93%) of groundwater samples had less than $5 \mu\text{g}\cdot\text{As L}^{-1}$, however, approximately 2% of the samples had concentrations $> 10 \mu\text{g}\cdot\text{As L}^{-1}$, and 5% had concentrations $5\text{-}10 \mu\text{g}\cdot\text{As L}^{-1}$ (Figure 2). The levels of As in Pennsylvania are similar to data reported from surrounding states. In another localized study, Shiber (2005) collected groundwater samples from private wells in Ohio, Kentucky and West Virginia and reported that 6% exceeded $10 \mu\text{g As}\cdot\text{L}^{-1}$.

The PA Department of Environmental Protection (DEP) sampled 940 groundwater stations, focused on the Southwestern, South central and Southeastern groundwater basins (Reese and Lee, 1998). Overall, the As concentration throughout the state averaged $4.2 \mu\text{g}\cdot\text{L}^{-1}$, and only 2 of the 940 samples (0.03%) collected were reported greater than the $50 \mu\text{g}\cdot\text{L}^{-1}$ standard (Reese and Lee 1998). The location of these two sampling sites was not reported, there was also no record of the proportion of samples with a concentration greater than $10 \mu\text{g}\cdot\text{L}^{-1}$.

There are some gaps in the data reported from the USGS. Of the 23 counties that comprise Western PA, 35% (8/23) had no groundwater data reported (Figure 2). In particular, there is little data from Northwestern PA, with no data available from Erie, Crawford, Mercer or Lawrence counties. Several areas in northern and northeastern Ohio have reported high As concentrations in groundwater (Welch *et al.* 2000), perhaps stemming the need for further study in those counties.

While approximately 600 samples were collected from 1978-1996, the majority of samples were collected from eastern PA. In particular, there were no samples reported from Allegheny County, perhaps due to the prevalence of treated drinking water within the county. There were 24 samples collected in the 5 counties surrounding Allegheny County (see Table 1). Of the 24, one sample (4%) was greater than $10 \mu\text{g}\cdot\text{L}^{-1}$ (Beaver County). A total of 29% of the samples (7/24) showed an As concentration in the range of 1-10 $\mu\text{g}\cdot\text{L}^{-1}$.

Arsenic in Allegheny County

The PA DEP groundwater study (1985-97) reported data from 46 groundwater basins, including 5 from southwestern PA. These five basins were clustered in Allegheny, Beaver and Westmoreland County. Overall, mean As concentration were between 3.9 and 4.5 $\mu\text{g}\cdot\text{L}^{-1}$ (Figure 3) (Reese and Lee, 1998). In 2001 a chemical analysis of surface water in the county (Shouse run) found 28 $\mu\text{g}\cdot\text{L}^{-1}$ (Koryak and Stafford, 2003), no local sources were identified in the study. Arsenic has been found locally in coal fly-ash deposits scattered throughout the county. Coal fly ash is a by-product of the coal fired power industry, this waste material has been dumped illegally at sites scattered throughout the state. In February 2005 a hill collapse in Forward Township brought coal fly-ash into the residential area directly below. The ash also entered surface waters that feed into the Monongahela River (1.81 mg As L⁻¹). The DEP found arsenic levels 170-268 mg kg⁻¹ in soil, 14 times the recommended level for soil cleanup in PA.

In 1988 the EPA reported groundwater concentrations ranging from 2.9 to 14.4 $\mu\text{g L}^{-1}$, and levels of arsenic in sediment of 9.7 mg kg⁻¹ in the Breslube Penn Inc. Superfund site. The site was operated from 1971-1986 as a solvent recovery and waste oil recycling facility. A freshwater stream that feeds into the Ohio River borders the site. The site contains by-products of waste oil including heavy metals, polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs). Surface waters were later measured in 1991 and found to have arsenic concentrations of 5.1 and 7.1 $\mu\text{g L}^{-1}$ (Lavin and Godfrey, 1997). To date this location remains on the NPL list of Superfund sites.

Lake sediments are useful archives of environmental pollution, and when dated can provide a local history of anthropogenic pollution (Smol, 2002). Panther Hollow Lake is a man-made reservoir located in the center of the city of Pittsburgh. A 49 cm long sediment core obtained in 2005 shows peak arsenic levels of 14 mg kg⁻¹ for the period 1950-1960, followed by a declining concentration after 1970. This decrease in sediment As is seen to occur around the decline of the local steel industry. An atmospheric flux ranging from 0 and 10 $\mu\text{g cm}^{-2} \text{yr}^{-1}$ was also observed indicating the presence of measurable non-point arsenic pollution in the last century (Cassidy, *Pers. Comm.*).

DETERMINATION METHODS

There are a variety of instrumental techniques for the determination of arsenic. These include both spectrometric (Hydride Generation Atomic Absorption Spectrometry, Colorimetry, Inductively Coupled Plasma – Atomic Emission Spectrometry, Inductively Coupled Plasma – Mass Spectrometry, UV/Vis Spectrophotometry) and electrochemical methods (voltammetry). Some of these (e.g. ICP-MS) can serve as speciation detectors when coupled to chromatographic separation techniques (e.g. HPLC and GC). Additional sensitivity for a limited range of arsenic compounds can often be achieved by the use of hydride generation techniques. These techniques have been thoroughly extensively reviewed by Hung *et al.*, 2004.

Recent surveys in Bangladesh (Pande, et al., 2001; Van Geen et al., 2005) and independent trials (Wagtech *Pers. Comm.*) have found colorimetric field test kits to be comparable to lab based measurements.

Colorimetry

The Gutzeit procedure involves the formation of arsine gas by reaction with sulfuric acid using zinc as a catalyst. The arsine is then reacted with either (i) mercuric chloride impregnated filter paper, the intensity of the black compound is compared with colors from standards treated with the same procedure, or (ii) silver diethyldithiocarbamate in pyridine to form a red color which is spectrophotometrically examined at 535 nm (Clescerl *et al.*, 1999).

A variation on the Gutzeit method is to absorb the arsine gas generated with sodium hypobromite which oxidizes the arsenic to arsenate. The arsenate reacts with ammonium molybdate in the presence of hydrazine sulfate for the formation of a heteropolymolybdenum blue complex. Arsenic is determined spectrophotometrically examined at 840 nm (Sandell, 1959). This method also provides the advantage of being able to identify and quantify arsenate and arsenite separately by generating arsine at different pHs.

Most test kits only report a range of concentrations. The Hach EZ-arsenic uses an updated version of the Gutzeit method. Sulfamic acid to zinc powder and ground water releases arsine gas that reacts with mercuric bromide to produce a color change. 0, 10, 25, 50, 100, 250, and 500 $\mu\text{g l}^{-1}$ concentrations are reported (Dhar et al., 2004). The Wagtech International digital arsenator is the most accurate colorimetric device available and utilizes a photometer to report in the range 2 to 100 $\mu\text{g l}^{-1}$.

Electrochemical

Detection using electrochemical technique involves the use of Cathode Stripping Voltammetry (CSV) at hanging mercury drop working electrode (Profumo *et al.*, 2005) with a limit of quantitation for As(III) 0.010 ppb and for As(V) 0.020 ppb. CSV reports in the range 2-32,000 $\mu\text{g l}^{-1}$. The limit of detection is 2 $\mu\text{g l}^{-1}$.

Hydride Generation Atomic Absorption Spectrometry (HG-AAS) Method

HG-AAS requires a pre-reductant step to convert all arsenic to As^{3+} . Arsenic is converted to its hydride (arsine) by sodium borohydride. The reduction to arsine gas provides a way of removing interferences and improves sensitivity by concentrating. The final step is atomization of the gas within a quartz cell (Thompson and Reynolds, 1978). Absorption is measured at 193.7 nm. HG-AAS reports in the range 5-50,000 $\mu\text{g l}^{-1}$. The limit of detection is 0.02 $\mu\text{g l}^{-1}$.

Graphite Furnace Atomic Absorption Spectrometry (GFAAS)

The amount of arsenic is determined directly at a wave length of 193.7 nm. As with HG-AAS the method of standard additions may be used where interferences are indicated. The limit of detection is 0.1 $\mu\text{g l}^{-1}$.

Inductively Coupled Plasma – Mass Spectrometry

This process uses the ion current measurement of monotomic $^{75}\text{As}^+$. Quantization is performed by normalizing to the ion current of ^{103}Rh , which is added as a 4 $\mu\text{g L}^{-1}$ standard. Chlorine interferes with arsenic via the formation of $^{40}\text{Ar}^{35}\text{Cl}^+$ and must be corrected for. This interference may cause the arsenic levels to be biased high by as much as 1 $\mu\text{g L}^{-1}$ for each 100 mg L^{-1} of chloride present. Even if corrections are being made to the results using the chlorine isotope ratio, these values may be inaccurate at the $\mu\text{g L}^{-1}$ level. The limit of detection is 0.2 $\mu\text{g L}^{-1}$.

CONCLUSION

Groundwater contamination by arsenic is one of the world's most serious environmental problems. At least 28 percent of Pennsylvanians depend on self-supplied groundwater as their main supply of water for domestic needs. When community (residential) and noncommunity (non-residential) water systems are included in a tally of groundwater users, the percentage of Pennsylvanians that use groundwater is around 50 percent. Contamination of groundwater by arsenic in any community's drinking water supply is a serious problem that requires further study.

An improved data-set of the concentrations of arsenic in ground waters can: (1) assist consumers reducing the risks of adverse health effects through avoidance or treatment; (2) provide a basis for evaluating the effectiveness of legislation in reducing the levels of this category one carcinogen in public drinking water supplies, (3) assist epidemiologists in evaluating models of arsenic intake from the natural environment. We hope to extend this research into the local community and assess the state of our local ground and surface waters

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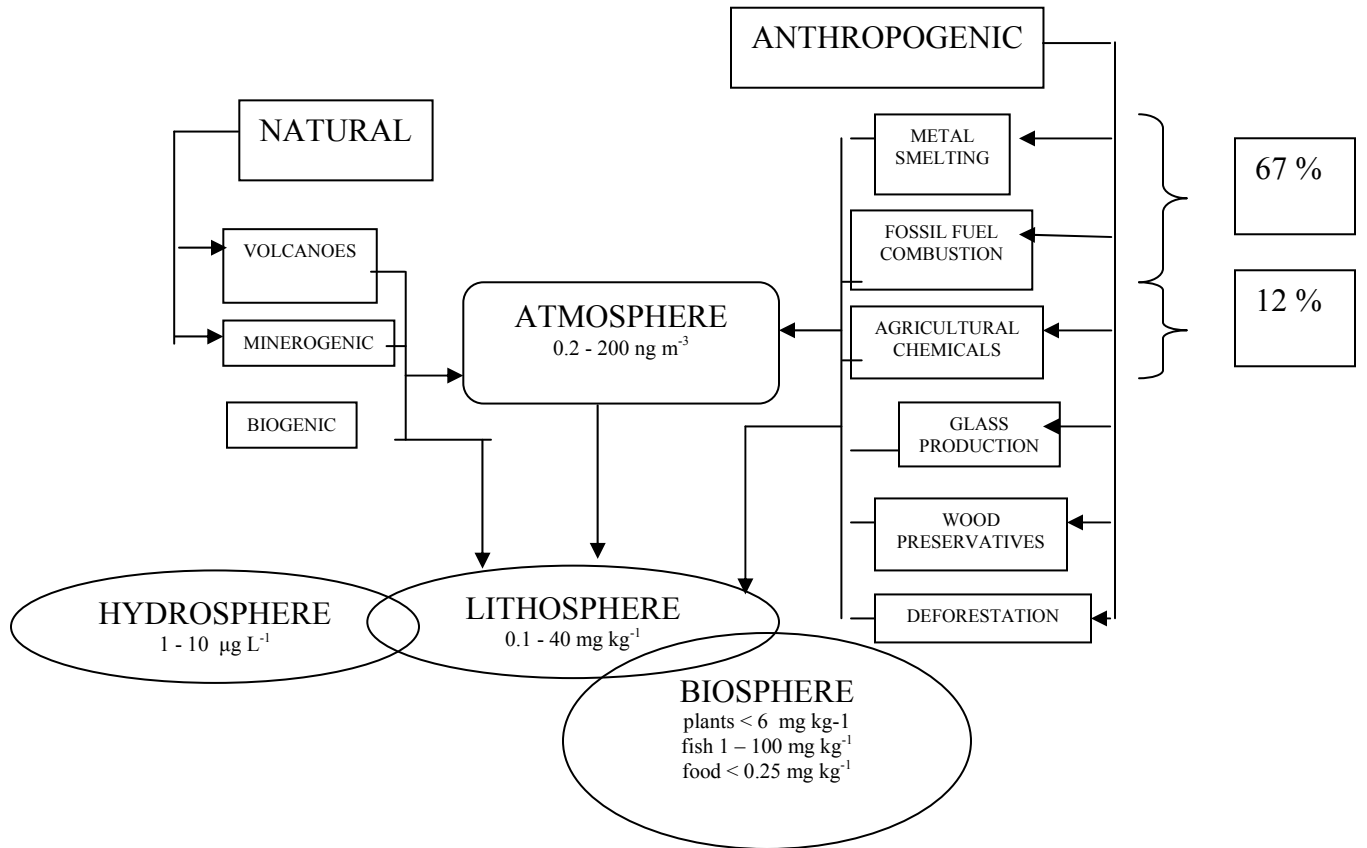


Figure 1: Major sources of arsenic in the environment including a summary of representative values. Data from Bennett, 1981.

Figure 2: As concentration ranges ($\mu\text{g}\cdot\text{L}^{-1}$) for Pennsylvanian counties sampled by the USGS.

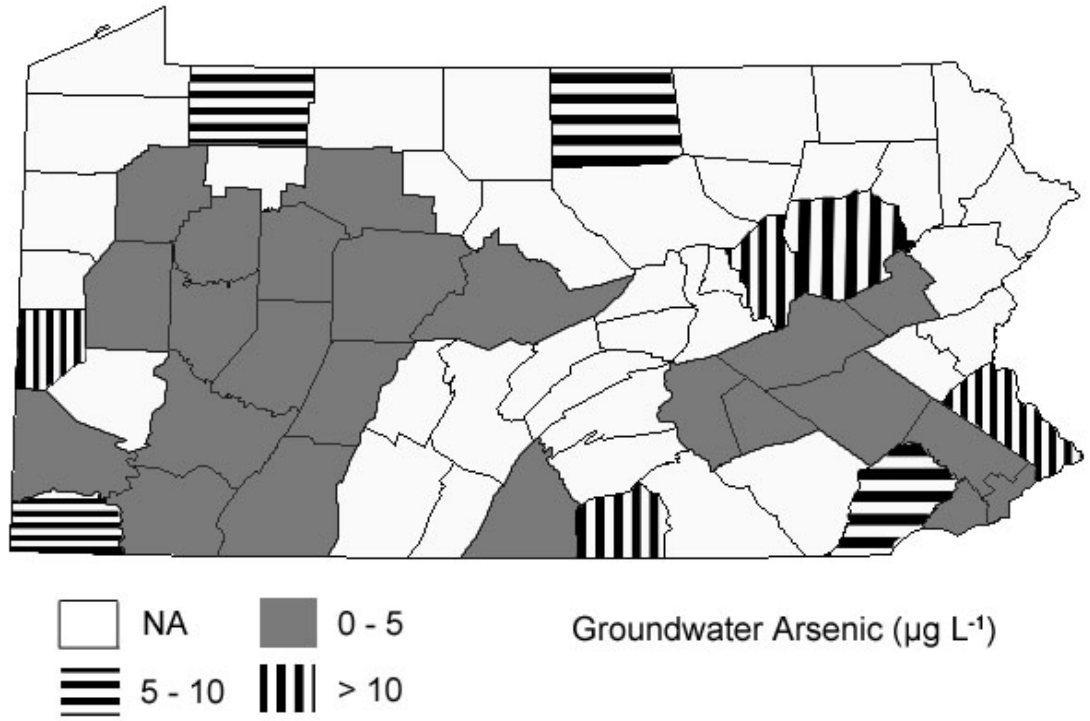
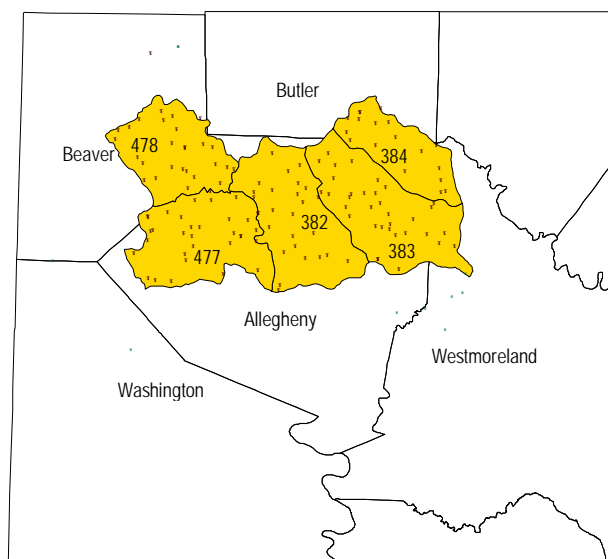


Figure 3: Location and mean As concentration ($\mu\text{g}\cdot\text{L}^{-1}$) for 5 groundwater basins sampled in the Pittsburgh region by the PA Department of Environmental Protection (figure reprinted from Reese and Lee 1998).



Groundwater Sampling Basin	Mean Arsenic Concentration ($\mu\text{g}\cdot\text{L}^{-1}$)
478	4.0
477	4.0
382	4.0
383	3.9
384	4.5

Table 1: Data reported from the USGS for As concentration in groundwater samples collected between 1979 and 1996 from 23 counties in western PA.

County	# Samples Collected	As Concentration Range ($\mu\text{g}\cdot\text{L}^{-1}$)
Allegheny	0	nd
Armstrong	3	< 1.0
Beaver	2	1.0-14.0
Butler	3	< 1.0
Cambria	2	< 1.0
Clarion	3	1.0-3.0
Clearfield	9	1.0-3.0
Crawford	0	nd
Elk	0	nd
Erie	0	nd
Fayette	3	< 1.0
Forest	0	nd
Greene	7	1.0-10.0
Indiana	11	< 1.0
Jefferson	41	< 1.0
Lawrence	0	nd
McKean	0	nd
Mercer	0	nd
Somerset	6	< 1.0
Warren	7	1.0-7.0
Washington	10	1.0-4.0
Westmoreland	6	< 1.0
Venango	1	< 1.0

nd = no data available

FOR LATER

Arsenic does not follow the book. It is an environmental toxicant, but often unrelated to industrial sources. It is a metal, but its metabolism involves organic modifications. It is an indisputable human carcinogen, but is largely negative in typical animal models of chemical carcinogenesis and its carcinogenic mechanism of action is a topic of great scientific debate. Oh, and by the way, arsenic is an excellent, anti-cancer pharmacological agent. (<http://coep.pharmacy.arizona.edu/arsenic/>)

PENNSYLVANIA GROUND WATER STUDY

Examples of states where they have a good idea of where the pollution is:

Massachusetts study

http://www.boston.com/news/local/massachusetts/articles/2005/01/19/concern_mounts_over_arsenic_in_wells/

IL study of well water

<http://www.sws.uiuc.edu/gws/arsenic/ilsources.asp>

Green county would be a good place to start see

<http://www.commondreams.org/news2004/1207-05.htm>.